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The Measurement of the Hydrolysis of Solutions of Sodium Salts of Fatty Acids. I.

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Introduction

THERE are two main problems in the study of the hydrolysis of soap solutions. The first is to establish the extent to which soaps are hydrolyzed in solutions under various conditions; and estimates have ranged from negligible amounts to 100% (1, 2). The second problem is to ascertain the products of hydrolysis. These have been variously assumed by different workers to be free fatty acid and free alkali, acid soaps of fixed or variable composition, and basic soaps.

The concept arrived at by McBain and his collaborators was that hydrolysis, though always present, yielding distinctly alkaline solutions even in the presence of excess fatty acid, is of minor extent except in the most dilute solutions. Of course, such dilute solutions are of importance in washing processes, and particularly in rinsing. The products of hydrolysis are taken as hydroxyl ion and one or more acid soaps of such composition as NaP:HP and 2NaP:HP, where P stands for a soap radical such as palmitate. Basic soaps are thought not to exist and free fatty acid is present only in extremely small amount, never enough even to equal its low solubility in water. Hence solid or liquid free fatty acid never separates out from soap solutions unless these are decomposed by carbonic acid or other acid.

In contrast some have assumed, without direct evidence, that free fatty acid as such is present in excess at all concentrations of soap solution. Ekwall (18) considers that this is only true in extreme dilution and Powney and Jordan (16) considered it untrue for dilute solutions and for concentrated solutions, but that free acid is present as such only in a range of moderate dilution.

Soaps were first studied extensively in 1823 by Chevreul (3); and in connection with the study of hydrolysis it was the investigation of the acid soaps deposited in dilute solutions with which he was concerned. Krafft from 1894 onwards studied the same phenomena (4).

In 1914 McBain and Martin measured the true hydrolytic alkalinity of pure soap solutions at 90° C. by means of the hydrogen electrode (1). The results of these experiments were confirmed by experiments of other kinds. McBain and Bolam in 1918 compared the catalytic effect of soap solutions on the decomposition of nitrosotriacetoneamine with those of known solutions of sodium hydroxide (5). McBain and Jenkins used the ultrafilter (6), McBain and Buckingham in 1927 (7) and McBain and Eaton in 1928 (8), measured the concentration of fatty acid in soap solutions by means of distribution experiments with non-aqueous solvents, and calculated the alkalinity. McBain, DuBois, and Hay in 1926 found the indicator method applicable to solutions of higher concentrations (9).

These experiments were interpreted in the light of the theory of colloidal electrolytes developed by McBain and set down in detail in 1920 in a paper by McBain and Salmon (10).

In 1927 McBain and Stewart prepared crystals of acid potassium oleate of the composition KOl:HOl from alcoholic solution (11). A large number of crystalline acid soaps have since been prepared by Ekwall and others (12), and in most cases conclusions from the results of analyses, melting point determinations, and x-ray studies (13) were that the acid soaps actually exist as crystalline compounds. Phase diagrams of various soap systems were studied by McBain and Field in 1933 (14). Ekwall in 1938 used a microscope equipped with a hot stage to examine the crystalline material suspended in soap solutions at different concentrations and temperatures, also analyzing the sediments (15).

The measurement of the degree of hydrolysis of soap solutions was taken up systematically in 1938 when Powney and Jordan obtained hydrolysis-concentration curves using the glass electrode (16) and when Stauff used the hydrogen electrode (17). Stauff used the curves as the basis of a new theory of hydrolysis which assumed association of fatty acid anions and hydrolysis of the associated anions to give the acid soap. This theory was made more extensive and complete by Ekwall in 1940 (18) who considered that it explained the hydrolysis-concentration curves he obtained for sodium laurate (19) and sodium caprate at 20° C. (20).

The present paper is concerned with the titration of acetic, lauric, and myristic acids in alcohol and in water; a later communication will record the pH values of a series of soap solutions at 25° C., the solubility of the higher fatty acids in water, and the extent to which all the aqueous soap solutions are unsaturated with regard to fatty acid.

Experiment and Discussion

Measurement of the pH of aqueous sodium acetate. First, decinormal solutions of Baker's Analyzed and of Kahlbaum's sodium acetate were prepared using boiled-out conductivity water, and they were found to have a pH of 8.0 at 25° C. The solutions were measured with a Beckman pH 7.0 buffer. The accuracy of the meter was further checked by use of a 0.05 *N* potassium acid phthalate with a pH of 4.0 and an alkaline buffer solution made up from a Burrel buffer tablet with a specified pH of 10.30 at 30° C.

Next, titration curves were investigated as a means of finding the true pH of a sodium acetate solution. A beaker containing 25 ml. of the decinormal solution of sodium acetate slightly on the acid side was suspended in a 1-liter Dewar flask containing water at 25° C., then the calomel electrode and blue glass electrode assembly was lowered into the solution. Increments of 0.02 ml. of N/100 sodium hydroxide were added from a 5 ml. microburette and the pH measured after each addition. In the three titration curves thus made the point of inflection always occurred very near to pH 8.8. These values agree well with theory, which predicts a value of pH 8.88 for a decinormal solution at 25° C. if $K_w = 10^{-13.99}$ and $K_a = 1.8 \times 10^{-5}$, and 8.87 if $K_a = 1.75 \times 10^{-5}$. The result confirms that crystallized sodium acetate always contains a slight excess of acetic acid.

The acetate was then recrystallized, but the pH changed only slightly, measuring from 7.9 to 8.1 in the various trials. So it became evident that crystals of sodium acetate retain approximately 0.08% excess of acetic acid. The acid salt NaAc.HAc has been known since the early 19th century, and it may form an isomorphous series with NaAc.

Titrations of higher fatty acids and soaps. In a somewhat similar way titration curves were made for pure soaps in boiled-out aqueous and in boiled-out alcoholic solutions, beginning with fatty acids rather than salts. Only in the case of alcoholic solutions does the point of inflection coincide with the equivalence point. In aqueous solution of pure soap the point of inflection comes later, on the alkaline side, due to hydrolysis. Titrations made in aqueous alcoholic solution in the presence of phenolphthalein indicate that when the concentration is in the region of decinormal, the color change occurs almost exactly at the equivalence point. This justifies the choice of phenolphthalein as an indicator in determinations of the equivalent weight by titration in aqueous alcoholic solution containing a major proportion of alcohol. The color change indicated by phenolphthalein in alcohol at this concentration is shown to indicate the point of true equivalence of fatty acid and alkali.

The equivalent of myristic acid was obtained thus: a 0.2000 g. sample of the Kahlbaum myristic acid was dissolved in 22 ml. of 95% alcohol in a 50 ml. beaker, 5 drops of 1% phenolphthalein were added and the solution was titrated with 0.1255 *N* sodium hydroxide from a 10 ml. microburette. The equivalent weight was found to be 228.6; that of Eastman myristic acid was found to be 227.7. The correct value would be 228.36.

Titration curves in aqueous solution were carried out in this manner: Enough myristic acid to give 10 ml. of a decinormal solution was weighed into a 50 ml. beaker, 95% of the calculated amount of 0.1255 *N* sodium hydroxide (made from sodium and water) was added, the mixture was heated on a water bath until the acid dissolved. Then it was suspended in a 50° water bath, small increments of the base were added, the pH being measured after each addition with the Beckman meter as above. At first an atmosphere of nitrogen was used to keep out carbon dioxide but was later found unnecessary. The temperature regulator of the pH meter was set at 40°C. and the meter was then adjusted so that it read accurately the pH of the pH 7 buffers (6.97 at 50°). If the dial reading is x at 50°, $\text{pH} = 6.97 + \frac{313}{323}(x - 6.97)$. The pH at the equivalence point was found to be 9.3, while the point of maximum inflection on the titration curve was near pH 10.1.

Eastman lauric acid was titrated in a similar manner. The pH at the equivalence point was 9.2, but at the point of inflection was 9.74. For myristic acid the volume of base needed to reach the point of inflection was 6.2% of the volume needed to reach the equivalence point. For lauric acid 1.5% excess was needed to reach the point of inflection at 50°C., 1.9% excess at 28° and 1.6% excess at 26°. This verifies the displacement of the point of inflection due to hydrolysis in water. Eastman palmitic acid was titrated also, but since the soap began to crystallize out before the titration was complete, the results were of little quantitative value.

Titration curves were made for myristic and lauric acid in boiled-out 80% alcohol in the presence of phenolphthalein. To 0.2214 g. of purified myristic acid (kindly supplied by Dr. S. Lepovsky) in a 50 ml. beaker, 45 ml. of 95% ethyl alcohol (the amount calculated to give 80% at the equivalence point) were added, with 5 drops of phenolphthalein. Then 0.1030 *N* sodium hydroxide was delivered in small increments from a 10 ml. microburette, the pH was measured using the saturated calomel-blue glass electrode assembly, the pH meter being standardized as before. The point of inflection came almost exactly at the equivalence point at 9.44 ml. of base when the apparent pH was 10.30. The numerical results are given as an example in Table I and shown graphically in Figure 1. Similar titration curves were constructed for the very pure lauric acid of Prof. F. Francis and for Standard Oil Company naphthenic acids of acid numbers 171, 200 and 262.

TABLE I.

Titration of Lepkovsky Myristic Acid in 80% Alcohol at 27° C.

Ml. NaOH	pH	Ml. NaOH	pH
0	5.69	9.10	8.55
1.00	6.76	9.20	8.70
2.00	6.99	9.30	8.96
3.00	7.12	9.40	9.77
		Color change	
4.00	7.22	9.45	10.56
5.00	7.31	9.50	10.88
6.00	7.44	9.60	11.07
7.00	7.59	9.70	11.16
8.00	7.82	9.80	11.21
8.50	8.02	9.90	11.25
9.00	8.39	10.00	11.29

Choice of Solvent for Distribution Experiments. Distribution experiments provide a means for the independent determination of free fatty acids in the solution. The purpose of the distribution experiment is to determine the concentration of fatty acid at which a given soap is in equilibrium with a solution of its fatty acid in a suitable non-aqueous solvent at a known temperature. If the distribution ratio is known, the concentration of the fatty acid in the soap solution can be calculated. A suitable solvent is very important here. It should be immiscible with water, should not react with the soap solution, and

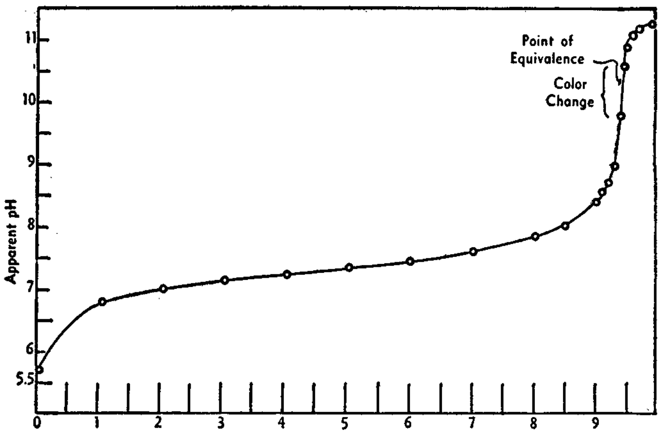

Fig. 1. Titration of a solution of 0.2214 gm. Lepkovsky myristic acid in 45.0 ml. 95% ethyl alcohol with 0.1030 N NaOH at 27° C. in the presence of five drops of 1% phenolphthalein, using the blue glass electrode.

should be only a moderately good solvent for the free fatty acid. A list of possible solvents was first investigated from this standpoint. For fairly volatile solvents this could be done by taking a known weight of a saturated solution at a given temperature, evaporating it, and weighing the residue. The results appear in Table II.

TABLE II.

Solvent	Temperature of measurements	$N_w = \frac{\text{mols HL}}{1000 \text{ g. solvent}}$
	°C.	
Isopentane	23	8.5
n-Hexane	23	3.8
n-Heptane	26	6.3
2,2,4-trimethyl pentane	26	3.5
Capryl alcohol	26	2.45
Benzene (c. p.)	26	8.3
Benzene (c. p.)	26	8.1
Carbon tetrachloride	26	5.1
Carbon disulfide	26	7.3
1-Nitropropane	26	1.2
2-Nitropropane	26	1.3
1,1-Chloronitropropane	26	0.80
n-Hexanol	26	4.5
Dihyexyl ether	26	2.9

Then a non-volatile mineral oil was tried; but a different technique was necessary. Weighed samples of mineral oil were enclosed in four-drum vials with weighed excess of Eastman lauric acid and shaken for several days in a 25° thermostat.

	Vial 1	Vial 2	Vial 3
	g.	g.	g.
Mineral oil	8.072	5.0769	4.2321
Lauric acid	1.24	2.4229	0.8658

Vial 1 dissolved completely while solid remained in the other two. Vial 3 was analyzed by titrating with alcoholic 0.0943 *N* sodium hydroxide a weighed amount, 1.7024 g., of the solution; isopropyl alcohol was added as solvent. A flocculent jelly formed during titration, making the end point uncertain. Using 13.95 ml. as the probable value,

$$N_w = \frac{13.95 \times 0.0943 \times 2003 \times 1000}{1.7024 \times 2003} = 0.773 \; N_w.$$

Mineral oil seemed the best solvent with respect to the solubility of lauric acid. Its obvious drawback is the difficulty of accurate analysis, but it is least likely to be solubilized by soap solution on account of its high molecular weight. However, Dr. Pierre Laurent later tried it as a solvent for the partition of fatty acid between it and aqueous soap solution and found the attainment of equilibrium prohibitively slow.

In past determinations of fatty acid concentration in soap solutions by distribution experiments, the distribution ratios of fatty acid between water and the solvent used was found for one concentration of soap by an indirect method and this value was assumed to hold for other concentrations. The hydroxyl ion concentration was measured and the concentration of free fatty acid was calculated from the equation:

$$\frac{C_{OH^-} \times C_{HA}}{C_{A^-}} = \frac{K_w}{K_a}$$

Knowing the concentration of fatty acid in the solvent solution in equilibrium with the aqueous solution, the distribution coefficient may be calculated.

Summary

1. pH values of recrystallized samples of sodium acetate, $NaAc.3H_2O$, measured with the Beckman pH meter at 25° C., using the "blue glass" electrode were near pH 8, rather than the calculated and true value for pure sodium acetate of 8.88. Titration curves were made beginning with decinormal solution of the slightly acid salt and adding sodium hydroxide; the pH at the inflection of these curves was near the correct value, 8.8.
2. Sodium hydroxide titration curves in aqueous solution were made at 50° C. for myristic acid and lauric acid, decinormal at the equivalence point. The point of inflection came after the equivalence point, giving the values of hydrolysis alkalinity for these two soaps.
3. Sodium hydroxide titrations in 80% alcohol at room temperature were made in the presence of phenolphthalein for Eastman myristic, Kahlbaum lauric, Lepkovsky myristic and the very pure Francis lauric acid. Concentrations at the equivalence point were about N/60. In every case the equivalence point, the point of inflection, and the color change coincided with the color change occurring near an apparent pH of 10.5 as indicated in alcohol.
4. The solubility of Eastman lauric acid was measured in a number of non-aqueous solvents at temperatures ranging from 23 to 26° C. Solubility was least in a sample of Braun-Knecht-Heimann medicinal mineral oil.

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